

**United States Department of Agriculture
Agricultural Marketing Service, Science & Technology
Pesticide Data Program**

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Title: MS Criteria		
Revision: 2	Replaces: 07/01/05	Effective: 01/01/07

1. Purpose:

To provide standard procedures for the identification, confirmation, and quantitation of pesticide residues determined by gas chromatography (GC) and liquid chromatography (LC) mass spectrometry (MS) and tandem mass spectrometry (MS/MS) for the USDA, AMS Pesticide Data Program (PDP).

2. Scope:

This standard operating procedure (SOP) shall be followed by all laboratories that utilize low resolution GC/MS, GC/MS/MS, LC/MS, and/or LC/MS/MS when conducting residue studies for PDP, including support laboratories conducting stability or other types of studies that may impact the program.

3. Outline of Procedure:

- 6.1 GC/MS
 - 6.1.a Apparatus and Materials
 - 6.1.b Reference Spectra
 - 6.1.c Minimum Requirements for Identification/Confirmation
- 6.2 GC/MS/MS
 - 6.2.a Apparatus and Materials
 - 6.2.b Reference Spectra
 - 6.2.c Minimum Requirements for Identification/Confirmation
- 6.3 LC/MS
 - 6.3.a Apparatus and Materials
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- 6.4 LC/MS/MS
 - 6.4.a Apparatus and Materials
 - 6.4.b Reference Spectra
 - 6.4.c Minimum Requirements for Identification/Confirmation
- 6.5 Dealing with exceptions
- 6.6 Documentation

Attachment 1 – Glossary of Mass Spectrometry Terms and Acronyms

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4. Narrative:

This SOP resulted from the desire to combine the requirements for all PDP MS and MS/MS procedures into a single document. Due to the complex nature of MS and MS/MS systems, these criteria cannot cover all possible scenarios. In those situations, a PDP laboratory can request an exception to the minimum requirements presented in this SOP.

5. References:

- USDA/AMS Quality Assurance/Technical Meeting, March 22-24, 2005, Manassas, VA
 - J.R. Chapman, Practical Organic Mass Spectrometry: A Guide for Chemical and Biochemical Analysis, 2nd Edition, John Wiley & Sons, West Sussex, UK, 1993
 - Food and Drug Administration Center for Veterinary Medicine, "Guidance for Industry: Mass Spectrometry for Confirmation of the Identity of Animal Drug Residues, Final Guidance," U.S. Department of Health and Human Services, Rockville, MD, Guide #118, May 1, 2003. <http://www.fda.gov/cvm/guidance/guide118.pdf>
 - K.L. Busch, "A Glossary for Mass Spectrometry," *Mass Spectrometry, Supplement to LC/GC*, 17 (6S), S26-S34 (2002)
 - Cairns and Siegmund, Regulatory Pesticide Analysis by Mass Spectrometry, Analytical Methods for Pesticides and Plant Growth Regulators, Vol. IV, pp. 193-253
 - J.A. Sphon, Use of Mass Spectrometry for Confirmation of Animal Drug Residues, *J. Assoc. Off. Anal. Chem.* 61 (1978) 1247-1252
 - U.S. EPA, 40 CFR 136, parts II, VI, and VIII
 - B.S. Middleditch, S.R. Missler, H.B. Hines, Mass Spectrometry of Priority Pollutants, Plenum Press, New York, 1981
 - R.A. Hites, Handbook of Mass Spectra of Environmental Contaminants, Lewis Publishers, Boca Raton, FL, 1992
 - R.A. Bethem, J. Boison, J. Gale, D. Heller, S. Lehotay, J. Loo, S. Mussler, P. Price, S. Stein, "Establishing the Fitness for Purpose of Mass Spectrometric Methods" *J. Am. Soc. Mass Spectrom.* 14 (2003) 528-541
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6. Specific Procedures:

This SOP represents the minimum PDP requirements and is presented as a general guideline. Each laboratory shall have written procedures that provide specific details concerning how the procedure has been implemented in their laboratory.

6.1 GC/MS

6.1.a Apparatus and Materials

6.1.a.1 Temperature-programmable GC complete with all accessories.

6.1.a.2 Capillary column which demonstrates acceptable chromatographic resolution.

6.1.a.3 Mass spectrometer (e.g., quadrupole, ion trap, time-of-flight) capable of scanning 20-500 atomic mass units (amu) in full scan mode and acquiring m/z abundance data in selected ion monitoring (SIM) mode for groups of three or more masses that are diagnostic to the target analyte(s).

6.1.a.3.a The mass spectrometer shall produce a mass spectrum capable of meeting all applicable reference spectra, identification/confirmation, and documentation requirements.

6.1.a.3.b When operated in the electron ionization (EI) mode, the mass spectrometer shall be capable of providing 70 electron volts (eV) as the ionization energy.

6.1.a.4 A computer system shall be interfaced with the GC/MS system that allows for data acquisition and storage of all mass spectra obtained throughout the duration of an analysis. The software shall include a library search option for EI acquired data.

6.1.b Reference Spectra

6.1.b.1 Tune Reference: The recommended tune procedure and/or program of the instrument manufacturer shall be used for instrument tuning. The manufacturer's

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specification for DFTPP, PFTBA, or other specified compounds shall be used to establish proper instrument tune parameters for the analytical run or acquisition time segment.

6.1.b.2 Standard Reference

6.1.b.2.a A MS reference spectrum for each target analyte shall be generated from a standard solution analyzed under the same instrument parameters that will be used for subsequent sample analysis. Reference spectra shall be archived and updated when it is determined that system response has changed due to different instrumental and/or operating conditions.

6.1.b.2.b Minimum documentation to be included with the reference spectrum includes: response, retention time, spectrum, ion abundances normalized to the base peak, date of injection, operator name, and instrument parameters under which the injection was made.

6.1.b.2.c Structurally significant ions used for confirmation/ identification shall be placed in a table that is referenced in laboratory SOPs.

6.1.c Minimum Requirements for Identification/Confirmation

6.1.c.1 Retention Time Criteria

6.1.c.1.a If an external standard is used, the retention time (RT) of the compound of interest in the standard and the RT of the same compound in the sample shall be ± 0.05 minutes. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

6.1.c.1.b If an internal standard is used, the relative retention time (RRT) of the compound of interest to the internal standard within the reference standard and the RRT of the compound of interest to the internal standard within the sample shall be within 0.01. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

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6.1.c.2 MS Criteria

6.1.c.2.a A minimum of three structurally significant ions (meeting the 3:1 s/n ratio) are required for identification, confirmation, and/or quantitation. Because the molecular ion is the most structurally significant ion in a mass spectrum, if it is present and meets the 3:1 s/n ratio, it is preferable, but not necessary, that it be included as one of the three ions.

6.1.c.2.b If obtaining three structurally significant ions is not possible due to limited fragmentation from “soft” ionization techniques, follow the procedures for dealing with exceptions (Section 6.5).

6.1.c.2.c Isotopic cluster ions may be used as one of the three structurally significant ions required for identification/confirmation.

6.1.c.2.d Use of fragment ions resulting from water loss to meet the three structurally significant ions requirement is discouraged.

6.1.c.2.e The confidence limits of the relative abundance of structurally significant ions used for SIM and/or full scan identification/confirmation shall be ± 20 percent (absolute) when compared to the same relative abundances observed from a standard solution injection made during the same analytical run.

6.1.c.2.f MS spectra produced by “soft” ionization techniques (e.g., chemical ionization) may require additional evidence for identification/confirmation. If the isotope ratio of the ion(s) or the chromatographic profile of isomers of the analyte is highly characteristic, there may be sufficient information for identification/confirmation. Additional evidence may consist of MS/MS data, use of a different ionization technique, and/or use of a different chromatographic separation system.

6.1.c.2.g Fragmentation that results from “soft” ionization techniques is highly dependent on instrument design and the conditions applied (i.e., the obtained spectra can widely differ). Commercially available spectral libraries bundled with GC/MS instruments contain spectra generated under standard 70eV EI conditions;

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therefore, the use of library search software for spectra from “soft” ionization techniques could result in identification errors and are discouraged.

6.1.c.3 QC Requirements

6.1.c.3.a Samples, standards, and blanks shall be analyzed using the same instrument conditions during the same analytical run.

6.1.c.3.b The laboratory shall develop internal procedures for performing an instrument air/water check.

6.1.c.3.c The laboratory shall develop internal procedures for monitoring tune profile and performing mass axis calibration.

6.1.c.3.d The laboratory shall evaluate and compensate, if necessary, for possible matrix effects such as ion suppression or enhancement that may affect sample analysis.

6.2 GC/MS/MS

6.2.a Apparatus and Materials

6.2.a.1 Temperature-programmable GC complete with all accessories.

6.2.a.2 Capillary column which demonstrates acceptable chromatographic resolution.

6.2.a.3 Mass spectrometer (e.g., triple quadrupole or ion trap) capable of scanning 20-500 amu in full scan mode and performing MS/MS, i.e., isolating an ion and subsequently causing it to undergo further dissociation in both full scan mode and selected reaction monitoring (SRM) mode.

6.2.a.4 A computer system shall be interfaced with the GC/MS/MS system that allows for data acquisition and storage of all mass spectra obtained throughout the duration of an analysis.

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6.2.b Reference Spectra

6.2.b.1 Tune Reference: The recommended tune procedure and/or program of the instrument manufacturer shall be used for instrument tuning. The manufacturer's specification for DFTPP, PFTBA, or other specified compounds shall be used to establish proper instrument tune parameters for the analytical run or acquisition time segment.

6.2.b.2 Standard Reference

6.2.b.2.a A MS/MS reference spectrum for each target analyte shall be generated from a standard solution to document the selection of appropriate target precursor and product ions. The reference spectrum shall be analyzed under the same instrument parameters that will be used for subsequent sample analysis. Reference spectra shall be archived and updated when it is determined that system response has changed due to different instrumental and/or operating conditions.

6.2.b.2.b Minimum documentation to be included with the reference spectrum includes: precursor ion, target ion, qualifier ion(s), precursor and product ion intensities, retention time, date of injection, operator, instrument parameters under which the injection was made, and the isolation and excitation parameters required to generate the product spectrum.

6.2.b.2.c Structurally significant ions and/or precursor-to-product ion transitions used for confirmation/identification shall be placed in a table that is referenced in laboratory SOPs.

6.2.c Minimum Requirements for Identification/Confirmation

6.2.c.1 Retention Time Criteria

6.2.c.1.a If an external standard is used, the RT of the compound of interest in the standard and the RT of the same compound in the sample shall be ± 0.05 minutes. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

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6.2.c.1.b If an internal standard is used, the RRT of the compound of interest to the internal standard within the reference standard and the RRT of the compound of interest to the internal standard within the sample shall be within 0.01. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

6.2.c.2 MS/MS Criteria

6.2.c.2.a Target analyte identification, quantitation, and confirmation shall be performed by either (1) monitoring the transition of one precursor ion to at least two product ions, OR (2) monitoring at least two precursor-to-product ion transitions. If instrument conditions and/or ionization techniques limit the number of precursor-to-product ion transitions, follow the procedures for dealing with exceptions (Section 6.5).

6.2.c.2.b The abundance of the signal from the precursor-to-product ion transition shall meet the 3:1 s/n ratio requirement.

6.2.c.2.c The confidence limits of the relative abundances of qualifier ion transitions to the target ion transitions in the sample shall be ± 20 percent (absolute) when compared to the same relative abundances observed from a standard solution analyzed during the same analytical run if more than one precursor-to-product ion transition is monitored.

6.2.c.2.d Use of product ions resulting from water loss for confirmation is discouraged.

6.2.c.3 QC Requirements

6.2.c.3.a Samples, standards, and blanks shall be analyzed using the same instrument conditions during the same analytical run.

6.2.c.3.b The laboratory shall develop internal procedures for performing an instrument air/water check.

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6.2.c.3.c The laboratory shall develop internal procedures for monitoring tune profile and performing mass axis calibration.

6.2.c.3.d The laboratory shall evaluate and compensate, if necessary, for possible matrix effects such as ion suppression or enhancement that may affect sample analysis.

6.3 LC/MS

6.3.a Apparatus and Materials

6.3.a.1 LC with a programmable solvent delivery system complete with all accessories.

6.3.a.2 LC column which demonstrates acceptable chromatographic resolution.

6.3.a.3 Mass spectrometer (e.g., quadrupole, ion trap, time-of-flight) capable of scanning 50-1200 amu in full scan mode and acquiring m/z abundance data in SIM mode for groups of three or more masses that are diagnostic to the target analyte(s).

6.3.a.3.a The mass spectrometer shall produce a mass spectrum capable of meeting all applicable reference spectra, identification/confirmation, and documentation requirements.

6.3.a.4 A computer system shall be interfaced with the LC/MS system that allows for data acquisition and storage of all mass spectra obtained throughout the duration of an analysis.

6.3.b Reference Spectra

6.3.b.1 Tune Reference: A suitable pesticide, or related compound, shall be used to establish optimized instrument tune parameters for the analytical run or acquisition time segment.

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6.3.b.2 Standard Reference

6.3.b.2.a A MS reference spectrum for each target analyte shall be generated from a standard solution analyzed under the same instrument parameters that will be used for subsequent sample analysis. Reference spectra shall be archived and updated when it is determined that system response has changed due to different instrumental and/or operating conditions.

6.3.b.2.b Minimum documentation to be included with the reference spectrum includes: response, retention time, spectrum, ion abundances normalized to the base peak, date of injection, operator name, and instrument parameters under which the injection was made.

6.3.b.2.c Structurally significant ions used for confirmation/ identification shall be placed in a table that is referenced in laboratory SOPs.

6.3.c Minimum Requirements for Identification/Confirmation

6.3.c.1 Retention Time Criteria

6.3.c.1.a If an external standard is used, the RT of the compound of interest in the standard and the RT of the same compound in the sample shall be ± 0.5 minutes. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

6.3.c.1.b If an internal standard is used, the RRT of the compound of interest to the internal standard within the reference standard and the RRT of the compound of interest to the internal standard within the sample shall be within 0.1. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

6.3.c.2 MS Criteria

6.3.c.2.a A minimum of three structurally significant ions (meeting the 3:1 s/n ratio) are required for identification, confirmation, and/or quantitation.

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6.3.c.2.b If obtaining three structurally significant ions is not possible due to limited fragmentation from “soft” ionization techniques, follow the procedures for dealing with exceptions (Section 6.5).

6.3.c.2.c If present, either the protonated or deprotonated molecular ions shall be used as one of the three structurally significant ions required for identification/confirmation as long as the 3:1 s/n ratio requirement is met.

6.3.c.2.d Isotopic cluster ions may be used as one of the three structurally significant ions required for identification/confirmation.

6.3.c.2.e Only one molecular adduct ion within each of the positive or negative ion modes may be used to meet the three structurally significant ions requirement.

6.3.c.2.f Use of fragment ions resulting from water loss to meet the three structurally significant ions requirement is discouraged.

6.3.c.2.g The confidence limits of the relative abundance of structurally significant ions used for SIM and/or full scan identification/confirmation shall be ± 20 percent (absolute) when compared to the same relative abundances observed from a standard solution injection made during the same analytical run.

6.3.c.2.h MS spectra produced by “soft” ionization techniques (e.g., APCI, APPI, ESI, etc.) may require additional evidence for identification/confirmation. If the isotope ratio of the ion(s) or the chromatographic profile of isomers of the analyte is highly characteristic, there may be sufficient information for identification/confirmation. Additional evidence may consist of MS/MS data, use of a different ionization technique, altering fragmentation by changing ionization conditions, and/or use of a different chromatographic separation system.

6.3.c.3 QC Requirements

6.3.c.3.a Samples, standards, and blanks shall be analyzed using the same instrument conditions during the same analytical run.

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6.3.c.3.b The laboratory shall develop internal procedures for monitoring tune profile and performing mass axis calibration.

6.3.c.3.c The laboratory shall evaluate and compensate, if necessary, for possible matrix effects such as ion suppression or enhancement that may affect sample analysis.

6.4 LC/MS/MS

6.4.a Apparatus and Materials

6.4.a.1 LC with a programmable solvent delivery system complete with all accessories.

6.4.a.2 LC column which demonstrates acceptable chromatographic resolution.

6.4.a.3 Mass spectrometer (e.g., triple quadrupole or ion trap) capable of scanning 50-1200 amu and performing MS/MS, i.e., isolating an ion and subsequently causing it to undergo further dissociation in both full scan mode and SRM mode.

6.4.a.4 A computer system shall be interfaced with the LC/MS/MS system that allows for data acquisition and storage of all mass spectra obtained throughout the duration of an analysis.

6.4.b Reference Spectra

6.4.b.1 Tune Reference: A suitable pesticide, or related compound, shall be used to establish optimized instrument tune parameters for the analytical run or acquisition time segment.

6.4.b.2 Standard Reference

6.4.b.2.a A MS/MS reference spectrum for each target analyte shall be generated from a standard solution to document the selection of appropriate target precursor and product ions. The reference spectrum shall be analyzed under the

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same instrument parameters that will be used for subsequent sample analysis. Reference spectra shall be archived and updated when it is determined that system response has changed due to different instrumental and/or operating conditions.

6.4.b.2.b Minimum documentation to be included with the reference spectrum includes: precursor ion, target ion, qualifier ion(s), precursor and product ion intensities, retention time, date of injection, operator, instrument parameters under which the injection was made, and the isolation and excitation parameters required to generate the product spectrum.

6.4.b.2.c Structurally significant ions and/or precursor-to-product ion transitions used for confirmation/identification shall be placed in a table that is referenced in laboratory SOPs.

6.4.c Minimum Requirements for Identification/Confirmation

6.4.c.1 Retention Time Criteria

6.4.c.1.a If an external standard is used, the RT of the compound of interest in the standard and the RT of the same compound in the sample shall be ± 0.5 minutes. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

6.4.c.1.b If an internal standard is used, the RRT of the compound of interest to the internal standard within the reference standard and the RRT of the compound of interest to the internal standard within the sample shall be within 0.1. If this requirement cannot be met, follow the procedures for dealing with exceptions (Section 6.5).

6.4.c.2 MS/MS Criteria

6.4.c.2.a Target analyte identification, quantitation, and confirmation shall be performed by either (1) monitoring the transition of one precursor ion to at least two product ions, OR (2) monitoring at least two precursor-to-product ion transitions. If instrument conditions and/or ionization techniques limit the

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number of precursor-to-product ion transitions, follow the procedures for dealing with exceptions (Section 6.5).

6.4.c.2.b The abundance of the signal from the precursor-to-product ion transition shall meet the 3:1 s/n ratio requirement.

6.4.c.2.c The confidence limits of the relative abundances of qualifier ion transitions to the target ion transitions in the sample shall be ± 20 percent (absolute) when compared to the same relative abundances observed from a standard solution analyzed during the same analytical run if more than one precursor-to-product ion transition is monitored.

6.4.c.2.d Use of product ions resulting from water loss for confirmation is discouraged.

6.4.c.3 QC Requirements

6.4.c.3.a Samples, standards, and blanks shall be analyzed using the same instrument conditions during the same analytical run.

6.4.c.3.b The laboratory shall develop internal procedures for monitoring tune profile and performing mass axis calibration.

6.4.c.3.c The laboratory shall evaluate and compensate, if necessary, for possible matrix effects such as ion suppression or enhancement that may affect sample analysis.

6.5 Dealing with exceptions

When a compound cannot routinely meet the above criteria due to the nature of the compound or analytical system, the laboratory can request an exception. The request shall explain the exception and how the confirmation will be accomplished. All requests for exceptions shall be sent to the MPO Technical Director. The laboratory shall document and maintain the requests.

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6.6 Documentation

The following QA/QC documentation shall be kept.

6.6.a Spectral scans for air or water as a means to check for an air/water leak in GC systems.

6.6.b Electronic or hard copies of tuning profiles generated prior to sample analyses of any compound used for tuning.

6.6.c Log of all instrument maintenance such as repairs, source cleaning, replacement of inserts, septa, columns, etc.

6.6.d Copies of chromatograms (total ion chromatograms, reconstructed ion chromatograms, etc.) for samples, standards, and QA/QC samples shall be kept with the raw data package.

6.6.e Electronic or hard copies of the reference spectra.

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Revision 2

November 2006

Monitoring Programs Office

- General update

Revision 1

- Reformatted SOP sections according to analytical technique
 - Deleted reference standards and reagents section
 - Changed relative abundance criteria for GC/MS and LC/MS to ± 20 percent (absolute) for both full scan and SIM
 - Changed the relative retention time requirement for LC/MS and LC/MS/MS to 0.1
 - Changed the requirement for using the molecular ion as one of the three structurally significant ions in GC/MS determinations from directive to suggestive
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Adduct ion: Ion formed by the interaction of the molecular ion and another compound or element (e.g., ammonium, hydrogen, sodium, etc.) as a result of van der Waals forces.

Atmospheric pressure chemical ionization (APCI): Ionization process where an aerosol of sample solution is sprayed at atmospheric pressure into a heated region creating a reaction between a reagent ion and a neutral molecule to create a charged ionic form of the molecule.

Atmospheric pressure ionization (API): Ionization process carried out at atmospheric pressure by any of several procedures including a radioactive source, electrical discharges, light sources, and high voltage electric fields. The main types are APCI, APPI, and ESI.

Atmospheric pressure photo ionization (APPI): Ionization process where an aerosol of sample solution is sprayed at atmospheric pressure into an area with a light source creating a reaction between photons and a neutral molecule to create a charged ionic form of the molecule.

Atomic mass unit (amu): An arbitrarily defined unit in terms of which the masses of individual atoms are expressed. One amu is exactly 1/12 of the mass of an atom of the nuclide ^{12}C (the predominant isotope of carbon).

Base peak: The ion with the most intense peak in the mass spectrum (full scan). The relative abundance of the base peak is assigned a value of 100%, and the abundance of all other ions plotted in that reference spectrum are normalized to that value.

Chemical ionization (CI): Ionization process initiated by the reaction of a reagent ion and a neutral molecule to create a charged ionic form of the molecule.

Collision induced dissociation (CID): Process by which an isolated ion is fragmented, producing an MS/MS spectrum. CID is sometimes called collision activated dissociation.

Confidence limits: The upper and lower boundaries in the range of values which includes (with a pre-assigned probability called the confidence level) the true value of a parameter.

“Absolute” confidence limits: Confidence limits determined for relative abundances of structurally significant ions by adding \pm the pre-assigned confidence level. For example, an absolute confidence limit of 15%, for ion 149 with a relative abundance of 45%, the confidence interval would be 30% to 60%.

“Relative” confidence limits: Confidence limits determined for relative abundances of structurally significant ions by multiplying \pm the pre-assigned confidence level. For example, a relative confidence limit of 15% for ion 149 with a relative abundance of 45%, the confidence interval would be 38% $[45 \times (100 - 15) / 100]$ to 52% $[45 \times (100 + 15) / 100]$.

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Confirmation: Verification of a previous analyte identification that is performed by another analytical system.

Deconvolution: Process to extract clean spectra from a complex mixture of overlapping peaks using mathematical algorithms.

Diagnostic ion(s): Ion(s) used to identify and quantitate the target compound. Diagnostic ions include the molecular ion, characteristic adduct ions, characteristic fragment ions (structurally significant ions), and isotope ions.

Electron ionization (EI): Ionization process initiated by the interaction of the gas-phase molecule with an energetic electron to create a charged ionic form of the molecule. Electron ionization is sometimes called electron impact.

Electrospray ionization (ESI): Ionization process where a sample solution is pumped into a capillary which is held at high potential causing a reaction between a reagent ion and a neutral molecule to create a charged ionic form of the molecule. The solution emerges from the capillary as a mist which is sprayed at atmospheric pressure into the mass spectrometer.

Fragment ion(s): Ion(s) formed when the precursor or product ion fractures after undergoing CID. All fragment ion(s) are product ion(s), but not all product ion(s) are fragment ion(s)

Full scan: The practice of monitoring and recording a wide range of ion mass-to-charge ratios (m/z) produced following sample ionization.

Ion trap: Type of mass analyzer consisting of two end caps and a ring electrode forming a three-dimensional quadrupole that stores ions at its center. An additional electrical signal is used to selectively eject ions to an external detector.

Ionspray™ ionization: Pneumatically assisted ESI. Ionspray ionization is also called turbospray ionization.

Internal standard: A substance not contained in the test sample with physical and chemical properties as similar as possible to those of the target analyte to be identified. An isotope-labeled form of the target analyte can also serve as an internal standard. The internal standard is added to each test sample as well as to each calibration standard at the beginning of the analytical process and used in the quantitative determination of the target analyte by taking into account the recovery of the internal standard.

Matrix-assisted laser desorption ionization (MALDI): Ionization process where sample molecules are mixed with an excess of energy-absorbing matrix. The subsequent mixture is co-crystallized in a thin film on an inert support. Repetitive irradiation with a pulsed laser releases ions from the surface.

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Molecular ion: An ion formed by the removal or addition of one or more electrons to a molecule without fragmentation; the peak representing the ionized molecule that contains only the isotopes of greatest natural abundance.

Mass spectrometry (MS): Analytical technique used to identify compounds based on their chemical structures' fragmentation patterns. MS instruments are called mass spectrometers.

Mass spectrometry/mass spectrometry (MS/MS): A form of mass spectrometry whereby ions are separated according to their mass-to-charge ratio in the first stage and are then fragmented by collisionally-induced dissociation, and the resultant fragment ions separated and measured in the second stage. MS/MS is also referred to as tandem mass spectrometry.

MSⁿ: MS/MS reactions recurring over multiple steps.

MS spectrum: Graphical representation of ion intensity vs. m/z data at a single point in time.

MS/MS spectrum: Graphical representation of ion intensity vs. m/z data at a single point in time produced by an isolated mass undergoing CID.

Multiple reaction monitoring: Selected reaction monitoring for more than one precursor-to-product ion transition.

m/z: A ratio of mass-to-charge.

Precursor ion: An abundant, structurally significant ion selected from the full scan spectrum to be isolated and subsequently subjected to CID. A precursor ion may be a molecular ion or a fragment ion. The precursor ion is sometimes called the parent ion.

Precursor ion scan: The practice of using the second stage mass analyzer in an MS/MS experiment to select a specific product ion and then using the first stage mass analyzer to scan for the precursor ion(s). The term parent ion scan is also used.

Product ion(s): Ion(s) formed from the reaction of the precursor ion. The reaction need not involve fragmentation through CID (e.g., the reaction involves a change in the number of charges carried by the precursor ion). If the reaction does involve CID, the product ion is also a fragment ion. Product ion(s) are sometimes called daughter ion(s).

Product ion scan: The practice of using the first stage mass analyzer in an MS/MS experiment to select a specific precursor ion and then using the second stage mass analyzer to scan for the resulting product ions. The term daughter ion scan is also used.

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Quadrupole: Type of mass analyzer consisting of four parallel rods arranged in a square array. Radio frequency and direct current voltages are applied to the rods creating a hyperbolic field that filters ions based on their mass-to-charge ratio.

Qualifier ion(s): Structurally significant ion(s) chosen from the reference spectrum to show consistent relative abundances when compared to the target ion. Qualifier ion(s) are sometimes called secondary ion(s).

Quantitation ion: A structurally significant ion that demonstrates a linear response over a broad range of concentrations. It is typically the target ion.

Reconstructed ion chromatogram: A plot of the intensity of specific ions in a MS or MS/MS spectrum (based on m/z) versus time.

Reference spectrum: Graphical representation of ion intensity vs. m/z data at a single point in time.

Relative abundance: The abundance of an ion relative to that of the most abundant ion, or base peak, in the spectrum.

Selected ion monitoring (SIM): Data acquisition technique of monitoring and recording one or more ion mass-to-charge ratios (m/z) rather than monitoring and recording the full MS spectra (i.e., a wide range of m/z values). This technique can greatly improve instrument sensitivity, albeit at a cost of reduced specificity. The term single ion monitoring is sometimes used.

Selected reaction monitoring (SRM): The MS/MS techniques of monitoring and recording one or more precursor-to-product ion transitions rather than monitoring and recording the full MS/MS spectra (i.e., all precursor or product ions). This practice can serve to greatly increase signal-to-noise by reducing noise.

“Soft” ionization: Low energy ionization process that typically results in little or no molecule fragmentation. The ions are usually either protonated ($M+H$)⁺ or deprotonated ($M-H$)⁻. Soft ionization processes include (but are not limited to) CI, ESI, APCI, and APPI.

Structurally significant ion: Ion with a mass-to-charge ratio (m/z) which indicates a characteristic structural grouping formed by the fragmentation of a molecule.

Target ion: A structurally significant ion selected from the reference spectrum, typically the most abundant ion, to be used to generate relative abundance ratios with qualifier ions. The target ion is sometimes called the primary ion.

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Time-of-flight (TOF) mass analyzer: Type of mass analyzer that uses the flight time of an ion over a fixed distance to measure its mass. Lower mass ions will move through fixed distance faster than higher mass ions.

Total ion current: A plot of the summed intensity of all acquired ions in a MS or MS/MS spectrum versus time. The term total ion chromatogram is also used.